CD221. LECTURE 1. INTRODUCTION

Thermodynamics deals in the broadest possible way with the phenomenon of *change*. More specifically, it deals with questions of the following kind:

> What happens when something interacts with something else?

There are lots of questions of this kind. For instance,

> What happens when you open the lid of a thermos flask containing hot coffee?
> What happens when you place a cup of water in a freezer?
> What happens when you prick the side of an inflated balloon with a pin?

All of the situations described by these questions have several common features:

(1) They all refer to objects or things of macroscopic dimensions, objects, in other words that are fairly large, large enough to be seen with the naked eye, and that are therefore made up of lots and lots of atoms.

(2) They all involve an event that separates objects into what can be thought of as two temporal domains, one that holds "before" the event, and one that holds "after". In the first situation, for example, this event is the opening of a lid. Before it takes place, the liquid in the thermos exists in one kind of condition, and afterwards, it exists in another. The opening of the lid makes it possible for something that was previously isolated to come into contact with the outside world.

(3) They all involve fairly well-defined – or at any rate well-characterizable – changes to some aspect of the before and after condition of the objects that interact. The liquid in the sealed thermos is hot, the liquid in the open container is cool.

These examples tell you that thermodynamics is the study of *material transformations*, transformations that alter the character of matter in the bulk. In fact, by thinking long enough about these and other examples of the above kind, you can say – or propose, as Callen does – that thermodynamics actually reduces to answering the following all-encompassing question:

> **What is the equilibrium state that results from the removal of internal constraints from a closed composite system?**

It probably won't be immediately obvious how this question represents the essence of any thermodynamic enquiry, and we won't be able to show that it does until we've given precise meaning to the various terms that appear in it. We'll provide those meanings later. In the meantime, keep this question in the back of your mind, and think of it as a kind of working hypothesis.

Now that we have a rough idea of what thermodynamics is, and what kind of questions it's interested in, we can turn to statistical thermodynamics. Statistical thermodynamics is interested in the same kinds of questions, but it's also interested in another question, which is the following:

Why does something happen when something interacts with something else?

If we answer this question we can say we've understood something of the basis for thermodynamics and the nature of its underlying causes. In this respect, statistical thermodynamics can be seen as the foundation of thermodynamics.

The way we'll try and answer the above question is by looking at a series of very simple situations that we believe we can understand completely or at least in great detail, and then use this understanding to formulate general principles that we hope will be applicable to essentially any other situation.

To implement this approach, it's important, as a first step, to be less colloquial in the way we use words, and to introduce precisely defined terms that have a wide and general applicability, and that are unambiguous in their meaning. A few of the new terms we'll now starting using are the following (we'll expand this list as we go along):

System. Any part of the physical universe we're interested in studying.

Surroundings. That part of the universe lying outside the system.

Boundary. The physical surface enclosing the system and separating it from the surroundings. Boundaries can be of several kinds:
   -- Rigid or moveable,
   -- Permeable (to matter flow) or impermeable or semi-permeable,
   -- Adiabatic or diathermal (we'll discuss the meaning of these terms later).

Closed system. One that is separated from the surroundings by a boundary that prevents any interaction between the two. A closed system is completely isolated from its surroundings, and produces no observable effect or disturbance on it. (N.B. This is Callen's definition of closed; other authors define a closed system as one in which no matter can pass through the boundary, though energy can, and an open system as one in which both energy and matter can pass through boundary.)

With these preliminaries, let's now look at a representative system whose behavior in the bulk and at the level of individual atoms or particles we can describe more or less completely. The system we'll look at for this purpose is a *dilute* gas of particles that is enclosed in a box and that is isolated from its surroundings by the walls of the box. Schematically, this is what the system might look like:

Of course, if the gas in question is something like Ar or He, you won't actually see the individual gas particles (as you do in the figure), but for the sake of argument we'll assume that we can.

The above system is one that we can describe or characterize at two levels. For instance, at one level – what we'll call the *microscopic* level – we know that the system is made up of particles that are in a state of perpetual motion, moving back and forth in the box, and constantly colliding with each other. If you were somehow able to take a snapshot of these molecules, so that for a single instant of time, they were all frozen in place, you might see something like this:
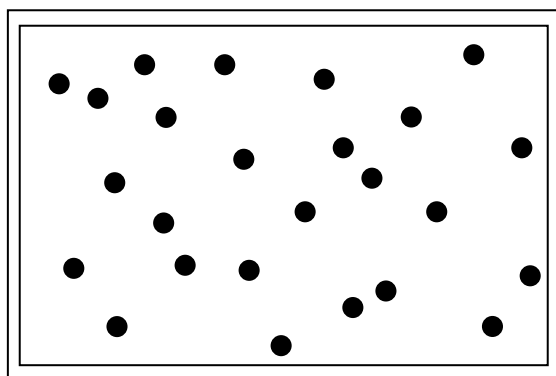

If you also had a way of labelling individual particles, you could say that in this instant of time particle 1 was at the coordinate (x_1, y_1, z_1), particle 2 was at coordinate (x_2, y_2, z_2) and so on. These coordinates provide about as detailed a description of the system as is practically possible.

At another instant of time, the gas particles would obviously no longer be in the above arrangement, but would have moved to new positions, leading to a configuration that might look like this:
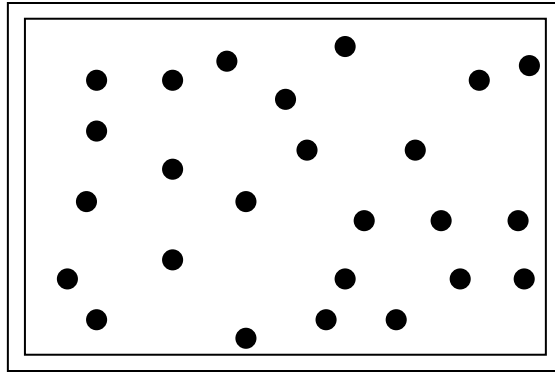
You can still describe the system by the coordinates of each of the individual molecules, but these coordinates are now different from the earlier ones. However, there's an important commonality to these two configurations. In each, the molecules are spread out randomly, but more or less uniformly, across the entire space available to them. And this would remain the case as you took more and more snapshots of the gas at successive instants of time. Only rarely would you encounter a situation like the one illustrated below:
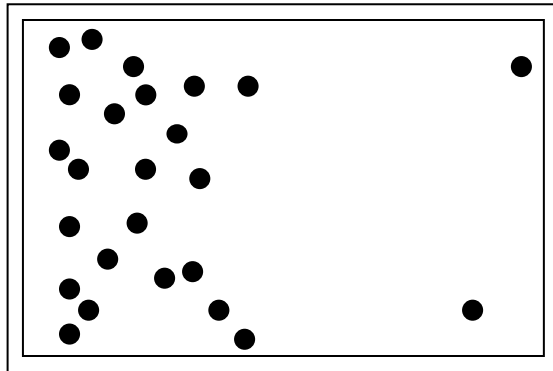

in which most of the molecules are located on one side of the box. This is especially the case when you have a large number of molecules in the box.

We can talk about this system at another level, what we'll call the *macroscopic* level. In a macroscopic description of the system, we ignore fine detail, like the positions of individual particles at different instants of time, and instead focus on a few gross features. In fact, at this level, it's not even strictly necessary to know that matter is made up of atoms and molecules. What would qualify as a gross feature of the system? We can identify one possible candidate if we mentally divide the box into two equal halves, as in the figure below:
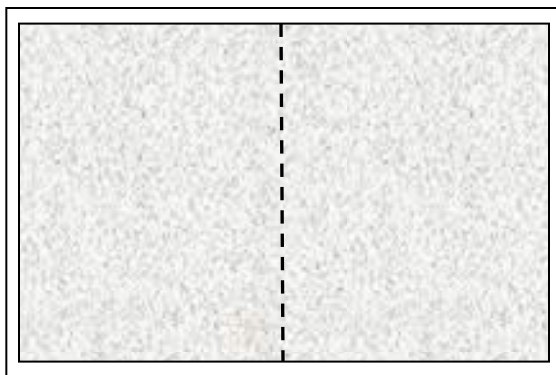
The *number* of molecules in each half of the box at a given instant of time (or possibly their mass) could then serve as a descriptor of the system at that instant of time. Let's call the number of molecules in the left of the box at time t $n_L(t)$. Suppose, furthermore, that the total number of molecules in the box is N, which is of course a constant. If you took a snapshot of the box at t, you'd almost certainly find that $n_L(t) \approx N/2$. And you'd find the same result if a series of snapshots of the box were taken at successive instants of time, provided N were fairly large. A graph of these numbers over the course of many such snapshots might look like this:
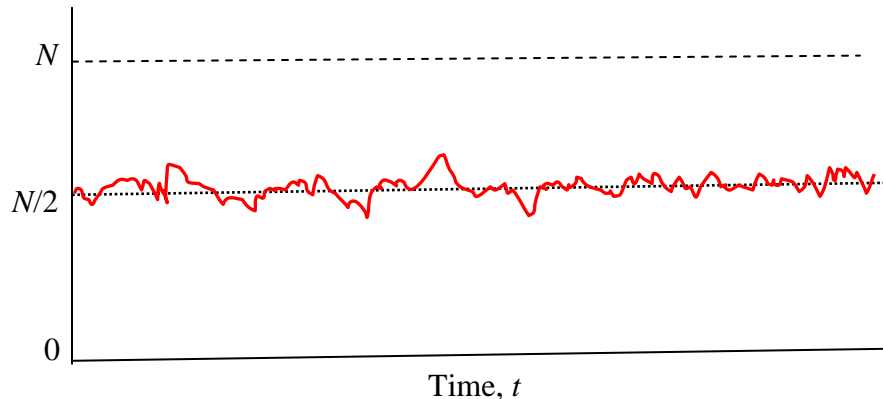
In other words, $n_L(t)$ makes minor excursions (in both the positive and negative directions) around the value of $N/2$, but is otherwise effectively a constant.

We would make roughly the same observations if we selected some other measure of the gross features of the system. For instance, instead of looking at the number of particles in the left half of the box, we could look at the *energy* of the particles in that half of the box, but not worry about which particle had what amount of energy. Suppose the total energy of the gas is, say, U. This energy is a constant, independent of time, because we've assumed that the box is isolated. It is equal to the sum of the kinetic and potential energies of all the N particles, but because we've also assumed that the gas is dilute

(which we did earlier on), the individual gas molecules are far apart from each other most of the time and mostly do not feel each other's presence, the energy U reduces effectively to just the kinetic energy. This kinetic energy comes from the particles' motion, i.e., from their velocities, which in general are all different, because the particles are all moving in different directions and with different speeds. But because they also collide with each other every now and then and with the walls of the box, they tend to share their energy with each other, so that over time and over the course of many such collisions, they end up with roughly the same energy. So the energy in the left of the box at any one instant of time will be about $U/2$, which comes from the approximately $N/2$ particles in that half of the box, each of which has roughly the same energy. There will, of course, be fluctuations around this value as particles move around and exchange energy with other, sometimes increasing the net total and sometimes decreasing it. So a graph of this energy as a function of time would look like the graph of $n_L(t)$ versus time.
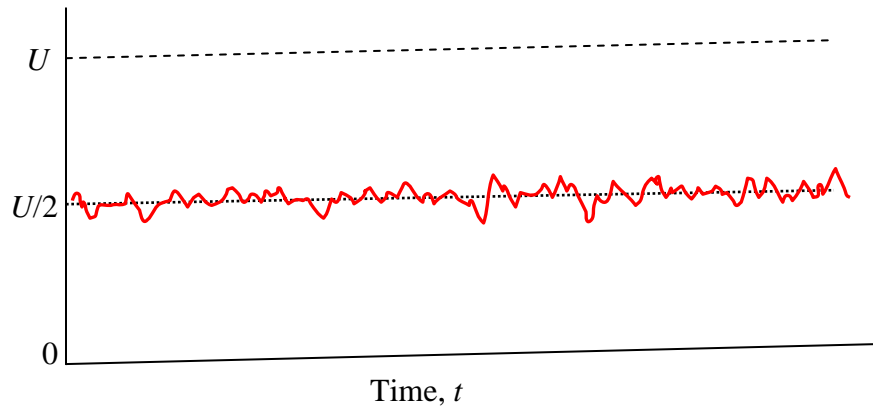
At the macroscopic level, then, this system, (and closed, i.e., isolated, systems more generally) exist in a condition that is adequately described by a few gross parameters that are essentially constant, independent of time, but that undergo small fluctuations around an average value. We'll call this condition *equilibrium*.

With these preliminaries, we're now in a position to start finding connections, if any, between the microscopic and macroscopic levels of description of a system. For this purpose we'll now introduce a few more new terms:

Properties of a system: These are the set of physical attributes that can be used to characterize the system at either the macroscopic or microscopic levels. The system is said to be in a definite *state* when these properties have definite values.

Macrostate: This is the state of a system when its macroscopic properties are specified.

Microstate: This is the state of a system when its microscopic properties are specified.

Let's now return to the example of an isolated gas in a box, but confine our attention for the moment to a gas with very few particles, so that we can talk about it in quantitative detail. To be specific, let's consider the case $N = 4$, and let's assume that at the *macroscopic* level, its state can be characterized by $n_L(t)$, the number of molecules in the left half of the box. Let's also assume that these 4 molecules are distinguishable, and have labels, say, 1, 2, 3 and 4. What macrostate would the gas be in if you took a snapshot of it at some instant of time? It could be in one of the following 5 macrostates:
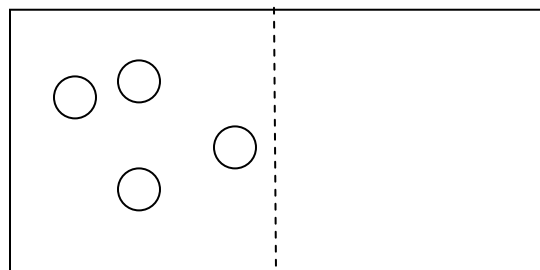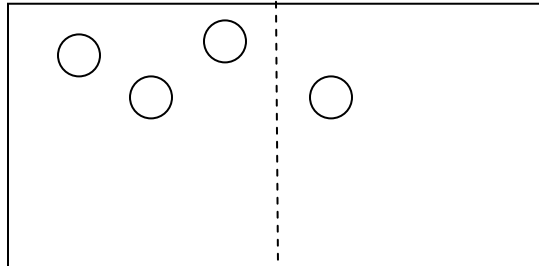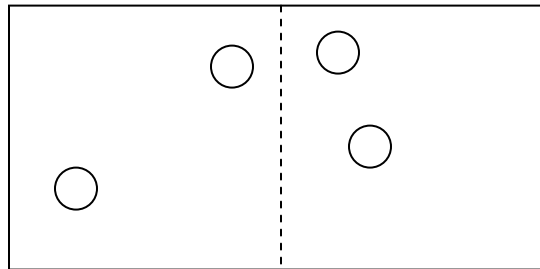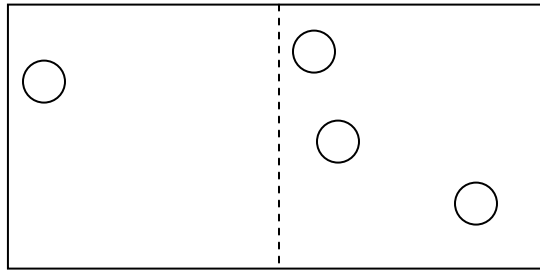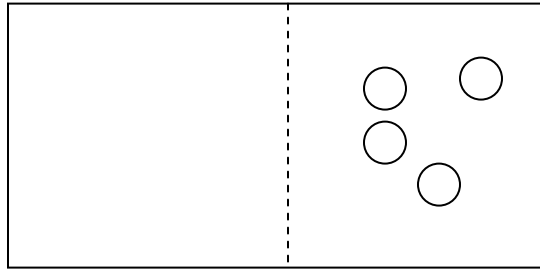
We obviously have no way of knowing à priori which of these macrostates it would be in at that instant of time, but we can make an informed guess. How do we do that? We do it by looking at the microstates of the system, which we can enumerate exhaustively. Take the case of macrostate 1, in which $n_L(t) = 0$. Clearly, there's only one possible arrangement of particles 1, 2, 3 and 4 that leads to this state. That is, a single microstate corresponds to the macrostate $n_L(t) = 0$. But there are 4 arrangements of 1, 2, 3 and 4 that correspond to the macrostate with $n_L(t) = 1$, and so there are 4 microstates that correspond to this macrostate. What about the macrostate $n_L(t) = 2$? To determine the corresponding number of microstates, we proceed as follows: There are 4 ways of placing one of the 4 particles in the empty left side of the box, and for each of these 4 possibilities there are 3 ways of picking the second particle to go into the box, for a total of 12 possible two-particle arrangements. But these 12 possibilities count as distinct, arrangements that differ only in the order of selection of the particles. That is, an arrangement like 1, 2 is taken to be different from 2, 1, whereas in fact it is not. So the number 12 has to be divided by the number of distinct permutations of two particles amongst themselves, which is 2. Which leaves us with 12/2 = 6 ways of placing 2 particles in the left side of box. Or in other words, the number of microstates corresponding to $n_L(t) = 2$ is 6. By the same reasoning, we find that the number of microstates corresponding to $n_L(t) = 3$ is 4, and the number corresponding to $n_L(t) = 4$ is 1. So in general, there are several different microstates for a given macrostate. Let's call the number of such microstates the *multiplicity* or *degeneracy* of the macrostate (symbol Ω), and let's now summarize the foregoing observations in the form of a table:

Macrostate $n_L(t)$	Microstate				Multiplicity Ω
	1	2	3	4	
0	R	R	R	R	1
1	L	R	R	R	
	R	L	R	R	4
	R	R	L	R	
	R	R	R	L	
2	L	L	R	R	
	L	R	L	R	
	L	R	R	L	6
	R	L	L	R	
	R	L	R	L	
	R	R	L	L	
3	L	L	L	R	
	L	L	R	L	
	L	R	L	L	4
	R	L	L	L	
4	L	L	L	L	1

So there are a total of 16 microstates that give rise to the 5 microstates of this four-particle system. Of these 16 microstates, the majority – 6 – correspond to macrostates in which the particles are equally distributed between the left and right halves of the box. If you happened to take 16 snapshots of the box at successive instants of time, the chances are that most of your photos would show 2 particles on the left and 2 on the right. We could be a bit more concrete about those chances if we knew how to assign definite probabilities p to each of these microstates. One way to do this is to define these probabilities in terms of the ratio of the number of times a sought-for event occurs to the number of times the events occur in toto. That is,

$$p(\text{macrostate}) = \frac{\text{number of favorable outcomes}}{\text{total number of outcomes}}$$

In other words,

$$p(n_L) = \frac{\Omega(n_L)}{\Omega_{\text{total}}}$$

where Ω_{total} refers to the sum of all the individual multiplicities, which in this case is 16. With this definition, and referring to the table above, we arrive at the following numbers

$$p(n_L = 0) = \frac{1}{16} = 0.0625 = 6.25\%$$

$$p(n_L = 1) = \frac{4}{16} = 0.25 = 25\%$$

$$p(n_L = 2) = \frac{6}{16} = 0.375 = 37.5\%$$

$$p(n_L = 3) = \frac{4}{16} = 0.25 = 25\%$$

$$p(n_L = 4) = \frac{1}{16} = 0.0625 = 6.25\%$$

What can we infer from these numbers? If we were somehow able to confine these 4 gas molecules to one side of the box by some kind of partition, and then removed the partition, so that the molecules could now wander freely across the entire volume of the box, after a long enough time, we'd find that they tended to populate the macrostate in which 2 gas molecules were on the left and two were on the right. In a crude sense, then, we can say that the removal of the constraint in this partitioned arrangement drives the system to a condition of greater uniformity.

This remark should call to mind what Callen proposes as the fundamental problem of thermodynamics, viz., **to determine the equilibrium state that results from the removal of internal constraints from a closed composite system.** It should be a little clearer now from the example above what this proposal means, and how we are to

interpret the terms internal constraint and closed composite system. Let's formally define these terms in the following way:

Internal constraint. Any boundary, real or imaginary, within a system that divides it into two or more parts, called *sub-systems*.

Composite system: A system divided in this way, by an internal constraint, into sub-systems.

Closed composite system: A composite system in which the sub-systems are initially isolated from each other but can be made to come into contact by the removal of an internal constraint such that the system as a whole continues to remain isolated from its surroundings.

With these definitions, you can probably begin to see that the questions we raised at the beginning of the lecture (such as, What happens when an inflated balloon is pricked?) describe situations where an internal constraint in a closed composite system is removed, and the system then settles into a new time-independent (equilibrium) state after the passage of a sufficiently long time. According to Callen, the essence of any thermodynamic problem is to determine the properties of this new equilibrium state.

Before we attempt to answer this question, let's sharpen our insights about the behavior of systems in general by looking at the macro- and microstates of the same enclosed gaseous system, but now having a 100 distinguishable particles instead of 4.